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(57) Abstract

The invention relates to a process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system which are isolable in the form of powder and which are soluble at a concentration of at least 100 mg atom of metal/l of water, from metal salts in the presence of strongly hydrophilic tensides with hydrotriorganoborates in THF, or with simple chemical reduction agents like hydrogen or alkali formate in water and alcohols, respectively. Furthermore, the subject matter of the invention is the use of the tenside-stabilized colloids which are produced according to this process as precursor for supported catalysts for the selective cis-hydrogenation of C-C triple bonds, for the selective hydrogenation of functional groups at the aromatic nucleus, for the selective hydrogenation of benzene to cyclohexene, for the partial oxidation of the primary alcohol functionality in carbohydrates, as well as for use as a precursor for electrocatalysts in fuel cells.

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Process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system in the form of precursors for catalysts which are isolable and water soluble at high concentration

Summary

The invention relates to a process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system which are isolable in the form of powder and which are soluble at a concentration of at least 100 mg atom of metal/l of water, from metal salts in the presence of strongly hydrophilic tensides with hydrotriorganoborates in THF, or with simple chemical reduction agents like hydrogen or alkali formate in water and alcohols, respectively. Furthermore, the subject matter of the invention is the use of the tenside-stabilized colloids which are produced according to this process as precursor for supported catalysts for the selective cis-hydrogenation of C-C triple bonds, for the selective hydrogenation of functional groups at the aromatic nucleus, for the selective hydrogenation of benzene to cyclohexene, for the partial oxidation of the primary alcohol functionality in carbohydrates, as well as for use as a precursor for electrocatalysts in fuel cells.

Description of the process

The use of colloidally stabilized one- and multi-metallic nanoparticles as separately isolable precursor for producing supported metal catalysts is a new, economically beneficial alternative to the traditional in situ formulation of active

metal components on carrier surfaces (H. Bönnemann et al., J. Mol. Catal. 86 (1994), 129-177]. The particular characteristic of the process according to the invention is the pre-formation of colloidally stabilized metal nanoparticles, optionally having an intermetalic composition, with defined size and particle structure. The characteristics of the catalyst (activity, selectivity, lifetime) of such metal colloids which are fixed on carriers are superior to conventional, supported catalysts.

The preferred solvent in this catalyst technology is water, due to economical and ecological reasons. The subject matter of the present invention is a process which permits to stabilize mono- and bimetallic nanoparticles in the form of powder in such a way, that highly concentrated colloidal solutions of the corresponding mono-and bimetallic catalyst-precursor can be produced in water without appreciable metal precipitations. By fixation of the precursor from aqueous solution on organic or inorganic carrier materials, new heterogeneous catalysts are prepared according the invention, for. e.g. selective hydrogenations, partial oxidations, or electrocatalysts for fuel cells.

According to the state of the art, some nanometals can be stabilized colloidally in water [T. Sato, S. Kuroda, A. Takami, Y. Yonezawa, H. Hada, Appl. Organomet. Chem. 1991, *5*, 261; T. Sato et al., J. Appl. Phys. 1990, *68*,1297; T. Sato et al., J. Chem. Soc., Faraday Trans. 1, 1987, *83*,1559; T. Sato, S. Kuroda, A. Takami, Y. Yonezawa, H. Hada, Appl. Organomet. Chem. 1991, *5*, 261; J. H. Fendler, "Membrane-Mimetic Approach to Advanced Materials", Springer-Verlag, Berlin, 1994; J. S. Bradley in "Clusters and Colloids", (Ed. G. Schmid), VCH, Weinheim 1994; H. Hirai, Y. Nakao, N. Toshima, Chem. Lett. 1978, *5*, 545; M. Ohtaki, M. Komiyama, H. Hirai, N. Toshima, Macromolecules 1991, *24*, 5567; N. Toshima et al., J. Phys. Chem., 1991, *95*, 7448; N. Toshima, T. Yonezawa, Makromol. Chem., Macromol. Symp., 1992,

59,327; N. Toshima et al., J. Phys. Chem. 1992, *96*,9927; K. Torigoe, K. Esumi, Langmuir 1993, *9*, 1664; J. S. Bradley et al., Chem. Mater. 1993, *5*, 254; H. Hirai, Y. Nakao, N. Toshima, Chem. Lett. 1976, *9*,905; M. Ohtaki, M. Komiyama, H. Hirai, N. Toshima, Macromolecules 1991, *24*,5567, N.Toshima, M. Ohtaki, T. Teranishi, Reactive Polym. 1991, *15*, 135; C. Larpent, F. Brisse-Le Menn, H. Patin, Mol. Catal. 1991, *65*, L35; N. Toshima, T. Takahashi, Bull. Chem. Soc. Jpn. 1992, *65*, 400-9].

However, the described metal colloids cannot be isolated, and they are soluble in water only at a high dilution. Therefore, they are not suitable as a catalyst precursor.

Some authors could isolate water soluble nanometal colloids in the presence of hydrophilic P- and N-donators [J. S. Bradley in "Clusters-and Colloids", (Ed. G. Schmid), VCH, Weinheim 1994; G. Schmidt, Chem. Rev. 1992, 92, 1709, H. Liu, N. Toshima, J. Chem. Soc., Chem. Commun. 1992,1095; C. Amberger, Ber. 1904, *37*,124; C. Paal, C. Amberger, Ber. 1905, *38*,1398].

Since P- and N-donators, being Lewis bases, give defined metal complex compounds with transition metals which, as is generally known, affects the catalytic efficiency of metals, the use of the mentioned complexing agent for the production of water soluble catalyst precursors is not suitable in the meaning of the present invention. Furthermore, the synthesis of these complexing agents occurs in several steps, and it is uneconomical.

Suitable auxiliary agents are known for stabilizing nanometals in water. Referring to this, also surface-active agents (tensides) were proposed by some authors [H. G. Petrow and R. J. Allen (Prototech Company), US-C 4,044,193 (1977); G. V. Lisichkin, A. Ya. Yuffa and V. Yu. Khinchagashvii, Russ. J. Phys. Chem., 50 (1976) 1285; V. M. Deshpande, P. Singh and C. S.

Narasimhan, J. Mol. Cat., 53 (1989) L21; V. M. Deshpande, P. Singh and C. S. Narasimhan, J. Mol. Cat., 63 (1990) L5; V. M. Deshpande, P. Singh and C. S. Narasimhan, J. Chem. Soc., Chem. Commun., 1990, 1181; Y. Nakao and K. Kaeriyama, J. Coll. and Surf. Sci., 110(1) (1986) 82; C. Larpent, F. Brisse-Le Menn und H. Patin, New J. Chem. 15 (1991) 361; K. Esumi, M. Shiratori, H. Ihshizuka, T. Tano, K. Torigoe and K. Meguro, Langmuir 7 (1991) 457; N. Toshima, T. Takahashi und H. Hirai, Chemistry Letters, 1985, 1245; N. Toshima and T. Takahashi, Chemistry Letters, 1988, 573; J. Kiwi and M. Grätzel, J. Am. Chem. Soc. 101 (1979), 7214]. However, the colloidal solutions of the corresponding metals in water are only stable at an extremely low concentration, not isolable and therefore, are discarded from the beginning as being used according to the invention as precursors for technical catalysts.

A significant progress in the production of water soluble metal colloids received Reetz and Helbig [M.T. Reetz, W. Helbig, J.Am.Chem.Soc. 1994, 116, 7401] by use of a LiCl salt of the sulfobetaine 3-(dimethyldodecyl-ammonio)propane sulfonate in an electrochemical reduction process. According to this electrochemical process, e.g., a good water soluble palladium colloid which is stabilized with sulfobetaine having a size of 8 nm, was isolated.

An economical alternative to the electrochemical production of nanometals is the chemical reduction of metal salts [H. Bönnemann et al.,Angew. Chem. Int. Ed. Engl. 29 (1990), 273; H. Bönnemann et al., J. Mol. Catal. 86 (1994), 129-177].

The use of commercial tensides for the stabilization of chemically-reductively produced nanometal colloids in highly concentrated aqueous solution could not be learned from the state of the art and from the ruling doctrine. On the contrary, surface-active substances are considered as auxiliary agents for

the precipitation of metals from aqueous solution. Surprisingly, it was found now that the chemical reduction of metal salts in the presence of extremely hydrophilic tensides leads to isolable nanometal colloids which form in an amount of at least 100 mg atom metal/l long-term stable solutions in water. The advantage according to the invention of extremely water soluble tensides for the stabilization of colloids illustrates the following comparison: Whereas the poor water soluble tenside $C_{16}H_{33}Me_3NBr$ (solubility according to Fluka catalogue 1993/94, CAS No. 57-09-0 = 0,1 mole/l of water) does not allow a stabilization of metal colloids in water according to the state of the art [G.V. Lisichkin, A.Ya. Yuffa and V.Yu. Khinchagashvii, Russ. J. Phys. Chem., 50 (1076), 1285], the use according to the invention of 3-(dimethyldodecyl-ammonium)propane sulfonate (solubility according to Fluka catalogue 1993/94, CAS No. 14933-08-5 = 1,2 mole/l of water) results in a solubility of the stable metal colloids of at least 100 mg atom/l of water.

Inorganic or organic salts of one or more metals from the groups VIII and Ib of the periodic system are dissolved, respectively suspended, in water or in a strongly solvated organic solvent (ether, THF, alcohols) in the presence of an extremely hydrophilic tenside, and they are reacted between 0°C and 100°C at environmental pressure, optionally by addition of alkali carbonate, with chemical reduction agents. Such reduction agents are, e.g., hydrogen, alkali formate, complex hydrides and other materials which are technically available for the reduction. The selection of the reducing agent will be determined, respectively, according to the reducing capacity which is necessary for the respective metal salt, as well as according to the stability of the used reagents in protic/aprotic solvents. As the extremely hydrophilic tensides, according to the invention, the following hydrophilic types of tensides can be used for the chemically-reductive preparation of colloids of mono- and bimetals of the groups VIII and Ib of the periodic

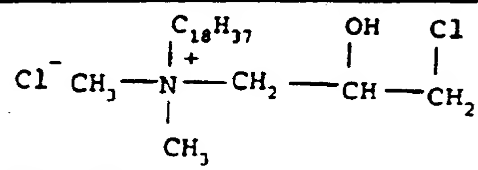
system in the form of isolable powders which are water soluble in high concentration (> 100 mg atom/l): amphiphilic betaines (A), cationic tensides (B), fatty alcohol-polyglycolether (C), polyoxyethylene-carbohydrate-fatty alkylester (D), anionic tensides (E) and amphiphilic sugar tensides (F).

The metal colloids which are prepared according to the invention as catalyst-precursor can be raised from aqueous solution to organic or inorganic carrier materials (e.g. activated carbon, graphitized carbon black, metal oxides) for the production of technically advantageously mono- and bimetallic heterogeneous catalysts. These heterogeneous catalysts which are prepared according to the invention are suitable for the selective cis-hydrogenation of C-C triple bonds (mono- and bimetallic Pd-colloidal catalysts on A-carbon), the selective hydrogenation of functional groups, as for instance $-NO_2$, at the aromatic nucleus (e.g, mono- and bimetallic Pt-colloid on A-carbon), for the selective hydrogenation of benzene to cyclohexene (e.g., Ru-colloid on La_2O_3), for the partial oxidation of the primary alcohol functionality in carbohydrates (e.g., Pd-, Pt-, Pd/Pt-colloids on A-carbon), or as electrocatalysts for fuel cells (e.g., Pt-colloid on graphitized carbon black).

Examples

The following types of tensides can be used according to the invention for the nanometal stabilization (table 1). The examples illustrate the invention without being limited thereby.

Table 1

hydrophilic type of tenside	name	tenside	name, formula, *commercial name*
A	amphiphilic betaines	A1	3-(N,N-dimethyldodecylammonio)-propane sulfonate (*SB12*)
		A2	Lauryldimethyl carboxymethyl-ammonium-betaine, *REWO*
		A3	Cocoamidopropyl betaine, *DEHYTON K*,
		A4	Cocoamidopropyl betaine, *AMPHOLYT JB130*,
B	cationic tensides	B1	 *QUAB 426*
		B2	$(R\overset{O}{\overset{\|}{C}}OCH_2CH_2)_n\underset{CH_3}{\overset{+}{N}}(CH_2CH_2OH)_{3-n}$ R = alkyl radical of partially hydrogenated palm grease *ESTERQUAT AU35*
C	fatty alcohol-polyglycolether	C1	polyoxyethylene laurylether, *BRIJ 35*
D	Polyoxyethylene carbohydrate-fatty alkylester	D1	polyoxyethylene sorbitan monolaurate, *TWEEN 20*
E	anionic tensides	E1	Na-cocoamidoethyl-N-hydroxyethyl glycinate, *DEHYTON G*
F	amphiphilic sugar tensides	F1	alkylpolyglycoside, *APG 600*

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with alkali BEt_3H in THF (see table 2).

Example 1

Ru-colloid (table 2, No. 4)

2.43 g (7.23 mmole) 3-(N,N-dimethyldodecylammonium)-propane sulfonate (tenside A1) are suspended under protective gas (argon) in 100 ml THF, and 5.60 ml of a 1,29 molar $LiBEt_3H$ solution in THF is added thereto at 20°C, whereby a clear tenside-reduction agent-solution results. This clear tenside-reduction agent-solution is dropped within 4 h at 40°C under stirring to a suspension of 0.5 g (2.41 mmole) $RuCl_3$ in 100 ml THF, and stirring is continued for further 16 h at 20°C. A grey-black precipitate and an almost colorless, supernatant solution are formed. After 2 h of settling, the supernatant solution is siphoned off, 5 ml acetone and 100 ml THF are added. It is stirred for about 10 min, and again the precipitate is allowed to settle during 1 h. The supernatant clear solution is siphoned off, and the precipitate is dried in high vacuum (10^{-3} mbar, 40°C, 1h). 0,65 g Ru-colloid in the form of a black solid having a Ru-content of 12.62% are obtained. Particle size according to TEM (transmission electron microscopy): 1-2 nm.

Physical characterization:

The colloids from experiments No. 5 and 26, table 2, were characterized by means of UV spectroscopy.

The XPS-spectrum of colloid No. 19, table 2 shows metallic platinum. The mean particle size was determined by means of TEM of the following colloids: No. 19: 2 nm; No. 20: 2,8 nm; No. 21: 3,7 nm (table 2).

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with alkali BEt_3H in THF (see table 3).

Example 2

Pt-Co-colloid (table 3, No. 3)

2.62 g (7.8 mmole) 3-(N,N-dimethyldodecylammonium)-propane sulfonate (tenside A1) are suspended under protective gas (argon) in 100 ml THF, and 6 ml of a 1,29 molar $LiBEt_3H$ solution in THF is added thereto at 20°C, whereby a clear tenside-reduction agent-solution results. This clear tenside-reduction agent-solution is dropped within 20 h at 20°C under stirring to a suspension of 0.78 g (2.93 mmole) $PtCl_2$ and 0.13 g (0.98 mmole) $CoCl_2$ in 120 ml THF, and stirring is continued for further 67 h at 20°C. A dark grey-brown precipitate is formed. 10 ml acetone are added, it is stirred for 1 h, and the precipitate is allowed to settle. The supernatant clear solution is siphoned off, and the precipitate is washed twice with 50 ml THF. After drying in high vacuum (10^{-3} mbar, 20°C, 1h) 2,84 g Pt-Co-colloid in the form of a black solid having a metal content of 17.6% Pt and 1,5% Co is obtained. Particle size according to TEM: 2-6 nm.

Physical characterization:

The colloids from experiments No. 4 and 6, table 3, were characterized by means of UV spectroscopy.

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with alkali metal boron hydrides in H_2O and alcohols, respectively (see table 4).

Example 3

Pt-colloid (table 4, No. 7)

2.7 g (5.3 mmole) H_2PtCl_6 x 6 H_2O and 3.6 g (10.6 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) are dissolved under the protective gas argon in 100 ml H_2O, and within 2 h a solution of 1.2 g (31.8 mmole) $NaBH_4$ in 50 ml H_2O are added thereto at 20°C. The resultant deep-black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C)

to dryness. 6.39 g Pt-colloid is yielded in the form of a black solid having a Pt content of 12,1%. Mean particle size according to TEM: 4,6 nm.

Physical characterization:
The colloid from experiment No. 2, table 3, was characterized by means of UV spectroscopy.

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with alkali metal boron hydrides in H_2O and alcohols, respectively (see table 5).

<u>Example 4</u>
Pt-Cu-colloid (table 5, No. 1)

1.35 g (2.65 mmole) H_2PtCl_6 x 6 H_2O and 0.11 g (0.66 mmole) $CuCl_2$ x H_2O are dissolved with 4.3 g (12.7 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) under protective gas (argon) in 100 ml H_2O, and within 2 h a solution of 0.38 g (17.0 mmole) $LiBH_4$ in 50 ml H_2O are added thereto at 20°C. The resultant deep-black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C) to dryness. 7.05 g Pt-Cu-colloid is yielded in the form of a black solid having a metal content of 7.02% Pt and 0,52% Cu. Particle size according to TEM: 2.5-4.5 nm; EDX-analysis: Pt:Cu = 1:0.2

Physical characterization:
The particle size of colloid no. 6, table 5 was determined by TEM: 3-5 nm; EDX-analysis: Pt:Ru = 1:1.05

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with hydrogen in H_2O (see table 6).

Example 5

Pt-colloid (table 6, No. 15)

1.4 g (5.3 mmole) $PtCl_2$, 7.2 g (21.2 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) and 0.4 g (5.3 mmole) Li_2CO_3 are taken up under a protective gas (argon) in 100 ml H_2O, and during 3 h a stream of H_2 is passed through this mixture at 20°C. A clear black solution is formed after approximately 30 min, from which all volatile matter is separated in high vacuum (10^{-3} mbar, 40°C). 8.4 g Pt-colloid is yielded in the form of a black solid having a Pt-content of 10.7%. Mean particle size according to TEM: 2.2 nm.

Annotation relating to operating the reaction:
Experiment no. 17, table 6 - deviating from the description of the above experiments - was performed in air.

Physical characterization:
The colloids from experiment nos. 1, 4, 5 and 6, table 6 were characterized by uv-spectroscopy.
The mean particle size of the following colloids was determined by TEM: no. 10:2.2 nm; no. 11:3.1 nm (table 6).

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with hydrogen in H_2O

Example 6

Pt-Pd-colloid

1.35 g (2.65 mmole) $H_2PtCl_6 \times 6\ H_2O$ and 0,7 g (2.65 mmole) $Pd(NO_3)_2 \times H_2O$ are dissolved together with 7 g polyoxyethyenelaurylether (tenside C1) and 1.0 g (13.25 mmole) Li_2CO_3 under a protective gas (argon) in 100 ml H_2O, and during 4 h H_2 gas is passed through it at 20°C. The resultant deep black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C)

to dryness. 11,2 g Pt-Pd colloid are obtained in the form of a black solid having a metal content of 4.3% Pt and 2.3% Pd.

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with Li-formate in H_2O

Example 7
Pt-Rh-colloid

1.35 g (2.65 mmole) $H_2PtCl_6 \times 6\ H_2O$ and 0,7 g (2.65 mmole) $RhCl_3 \times H_2O$ are dissolved with 7 g polyoxyethylene laurylether (tenside C1) under a protective gas (argon) in 150 ml H_2O, and during 20 h a solution of 2.86 g (55.0 mmole) Li-formate in 50 ml H_2O is added thereto at 60°C. The resultant deep black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C) to dryness. 12.5 g Pt-Rh colloid are obtained in the form of a black solid having a metal content of 4.0% Pt and 2.0% Rh.

Fixation of the carrier

Example 8
Preparation of a Pd-tenside A1/activated carbon catalyst for the partial oxidation of carbohydrates (5 percent per weight of Pd/C)

1.254 g of a microporous (< 5nm) powdery active carbon having a grain size of 20 μm are suspended in 50 ml deoxygenated H_2O, and 64.7 ml of a solution of Pd-colloid no. 16, table 2 in deoxygenated water (1.02 mg Pd/ml) are given thereto within 16 h under stirring. The covered active carbon is separated over a glas filter frit; yielding a colorless filtrate. It is washed twice with 25 ml deoxygenated water, respectively, and dried during 16 h in vacuum (10^{-3} mbar). Subsequently, the catalyst is oxygenated during 16 h at 0,1 mbar (approximately 0,2% O_2). The obtain d catalyst can be handled in air.

Example 9

Pr paration of a Pd-tenside A1/active carbon-catalyst for the selective hydrogenation of C≡C (5% per weight of Pd/C)

A solution of 0.7885 g (corresponding to 0.1053 g Pd) colloid no. 16, table 2 in 40 ml distilled water is dropped within 16 h under argon to 2.00 activated carbon (Degussa carrier material 101, charge 514) which was given in the form of a suspension in 40 ml water under argon. Thereby, the colloid is completely absorbed on the activated carbon which can be seen by the decoloration of the solution. The catalyst is filtered off, dried during 16 h at 20°C in high vacuum (10^{-3} mbar), and it is oxygenated during 16 h at 20°C at 0.1 mbar (approximately 0.2% O_2).

Example 10

Preparation of a Ru-tenside A1/lanthanumoxid catalyst for the selective hydrogenation of benzene (1 percent per weight of Ru/La_2O_3).

5.505 g La_2O_3 (BET surface area of 59 m^2/g) are suspended in 100 ml deoxygenated H_2O under a protective gas. Within 30 min 50 ml of a solution of Ru-colloid no.4, table 2 in deoxygenated H_2O (440 mg, EA: 12.62% Ru), is dropped thereto. Thereby, the white oxidic carrier changes to a grey colour. The complete absorption can be seen from the decoloration of the black solution. The coated carrier is allowed to settle completely, and the supernatant, clear aqueous solution is siphoned off. After drying in vacuum (10^{-3} mbar, 3 h), a grey powder is obtained which is stable in air.

Catalysis

Example 11

Use of a Pd-catalyst for the oxidation of glucose to gluconic acid.

100 ml of an aqueous solution of glucose with 16 g glucose (99 percent per weight) (88 mmole) and 0.24 g of the catalyst described in example 8 (1.5 percent per weight in relation to the amount of glucose) are transferred to a 250 ml stirring reactor equipped with gassing stirrer, thermometer, alkali metering, pH electrode and oxygen feeding. The oxygen is distributed at normal pressure by means of the gassing stirrer in the solution at a reaction temperature of 56°C. The resulting gluconic acid is neutralized by dropping 10 percent per weight of caustic soda thereto. Thereby, the pH value of the suspension is 10.0. The catalyst is filtered off, and the filtrate is analyzed by means of ion chromatography and HPLC.

Conversion (min): 49%
Selectivity (120 min): 92%
Activity (120 min): 327 g [gluconic acid]/g [Pd] x hour

Example 12

Use of a Pd-catalyst for the selective hydrogenation of 3-hexyne-1-ol to cis-3-hexene-1-ol

30.0 mg of a Pd-colloid/activated carbon catalyst, prepared according to example 9, are weighed in a 100 ml dropping funnel. The measuring of the selectivity is performed in a reactor which is thermostatted to -10°C. The dropping funnel is put upon the reactor, the whole apparatus is evacuated several times and flushed with hydrogen. Subsequently, the catalyst is placed into the reactor in hydrogen-counterflow with 100 ml of absolute, non-degenerated ethanol under argon in 2 portions of 50 ml, respectively. The dropping funnel is taken off and it is replaced by a septum. 10 ml 3-hexyne-1-ol are injected through the septum. After thermostatting the suspension at -10°C and

pressure compensation, the path to a 1 l-precision buret which is sealed by mercury is opened. GC samples are taken through the septum by means of a syringe with filter aid and hypodermic steel needle in regular intervals until stoichiometric hydrogen take-up is attained. Selectivity according to GC: 94.9%.

Example 13

Use of a Ru-catalyst for the partial hydrogenation of benzene to cyclohexene

10 ml benzene, 40 ml water with 3 g NaOH and 500 mg of the catalyst described in example 10 (1 percent per weight Ru/La_2O_3, 6.25 percent per weight of catalyst in relation to the amount of benzene) are filled into a 100 ml stainless steel autoclave. The content is stirred with the club stirrer and heated to 150°C. Now, it is pressed on to 50 bar of hydrogen pressure. The autoclave is taken from the heating jacket support after 30 min, and stirring is interrupted. Thereby, a hydrogen up-take of 18 bar can be noticed. The residual H_2 pressure is blown off after cooling, and a sample is taken from the upper organic phase which is examined by gas chromatography.

Conversion(benzene): 8.5%

Selectivity (cyclohexene): 78.5%.

Example 14

Preparation of a platinum colloid stabilized by dihydrocinchonidine

0.104 g $PtCl_4$ (0.31 mmole) are dissolved in a 100 ml two-neck flask, provided with reflux condenser and a septum, in 83 ml water, and heated to reflux temperature in an oil bath. The temperature of the oil bath is 140°C (±5°C) during the synthesis. A solution of 0.092 g dihydrocinchonidine (0.31 mmole) in 7 ml of 0.1 n formic acid is rapidly injected through the septum. In the beginning, the reaction mixture becomes turbid and begins to become black colored after some minutes. The reaction is finished approximately ten minutes after the

beginning of the black coloration. The reaction mixture is frozen in liquid nitrogen and liberated of water and the forming hydrochloric acid by freeze drying. A black powder is obtained which can be completely dispersed in water. If the formed platinum colloids should be applied on carrier materials, the aqueous product dispersion can be used without isolation of the metal particles before the application on the carrier. The yield is 0.18 g (103% of the theory) in this reaction. The elemental analysis shows 34.5% Pt, 16% Cl, 39.5% C, 5% H and 5% N. Electron-microscopic examinations show an average particle size of 2 nm.

Example 15

Preparation of a heterogeneous platinum catalyst by adsorption of platinum colloids on silicon dioxide and active carbon

100 ml of the colloid, described in example 14, are directly taken up after the synthesis in 100 ml cold, distilled water, and are dropped during one hour to 100 ml of the carrier suspension. Either the highly disperse silicon dioxide Aerosil P 25™ (Degussa) or the active carbon carrier 196 (Degussa) which was oxidized with sodium hypochloride before the application to the carrier, can be used as carriers. The obtained suspensions are stirred with a magnetic stirrer at a low rotational speed during two days, and they are susequently filtrated. The filtrate is completely discolored, a fact from which it can be concluded that the metal colloids were quantitatively absorbed on the carrier. The thus obtained heterogeneous platinum catalysts were dried in a drying oven, and they can be used subsequently as hydrogenation catalysts without further intermediary step. A uniform and agglomeration-free distribution of the colloids on the carrier materials could be proven by electron-microscopic examinations.

Example 16

Enantioselective hydrogenation of 2-keto-propane acid ethylester to 2-hydroxy-propane acid ethylester

A 100 ml autoclave is charged with the catalyst described in example 15 (platinum on silicon dioxide; metal content 5%), 5 ml 2-keto-propane acid ethylester (45 mmole), 20 ml dihydrocinchonidine (0.1 mmole), 10 ml acetic acid and a magnetic stirrer nucleous having a size of 3 cm. The presure vessel is degassed after being closed, and subsequently, 100 bar hydrogen are pressed on under vigoreous stirring. The reaction takes place at 20°C, and it is terminated approxiamtely after 15 minutes. Following the expansion of the pressure vessel, the product mixture is liberated of the catalyst by filtration, the clear filtrate is taken up in 180 ml saturated sodium bicarbonate solution and subsequently extracted three times with each 20 ml of diethyl ether. The combined organic phases are concentrated on a rotary evaporator, the remaining clear solution is examined by NMR spectroscopy and mass spectroscopy, and it is identified as 2-hydroxy-propane acid ethylester. The yield was determined by gas chromatography to 90%. The optical yield of the reaction was examined by gas chromatography on a chiral column, and yields an excess of enantiomer of 81%.

Table 2: Tenside stabilized colloids of metals of the groups VIII-Ib of the periodic system by reduction with alkali BEt_3H in THF

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
1	$NiBr_2$	C1	-	$LiBEt_3H$	THF	50	20	8,5	Ni: 2,9	110
	0,7/5,3	7/-		10,6	200					
2	$CoCl_2$	C1	-	$LiBEt_3H$	THF	50	20	8,3	Co: 3,1	120
	0,7/5,3	7/-		10,6	200					
3	$CuCl_2$	A1	1:4	$LiBEt_3H$	THF	20	48	9,02	Cu: 3,5	300
	0,71/5,3	7,2/21,2		10,6	500					
4	$RuCl_3$	A1	1:3	$LiBEt_3H$	THF	40	4	0,65	Ru: 12,62	310
	0,5/2,41	2,43/7,23		7,23	200					
5	$RuCl_3$	A2	1:3	$LiBEt_3H$	THF	40	2	0,23	Ru: 13,52	150
	0,21/1,04	0,85/3,13		3,13	100					
6	$RhCl_3$	A1	1:3	$LiBEt_3H$	THF	65	28	3,9	Rh: 25,21	320
	2,05/9,7	9,86/29,38		30,78	600					
7	$RhCl_3$	A1	1:2	$LiBEt_3H$	THF	40	34	1,91	Rh: 11,50	350
	0,45/2,15	1,443/4,3		6,45	105					
8	$RhCl_3$	A1	1:1	$LiBEt_3H$	THF	40	34	1,08	Rh: 20,4	370
	0,45/2,15	0,721/2,15		6,45	105					

Table 2: continuation 1

No.	Metal salt g/mmole	Tenside g/mmole	Metal salt/-tenside molar ratio	Reduction agent mmole	Solvent ml	Reaction conditions T, °C	t, h	isolated amount of product g	Metal content %	Water solubility in mg atom metal / l water
9	$RhCl_3$	A1	1:0,75	$LiBEt_3H$	THF	40	34	0,87	Rh: 25,2	410
	0,45/2,15	0,541/1,61		6,45	105					
10	$RhCl_3$	A1	1:0,5	$LiBEt_3H$	THF	40	34	0,67	Rh: 32,9	440
	0,45/2,15	0,361/1,075		6,45	105					
11	$RhCl_3$	A2	1:3	$LiBEt_3H$	THF	60	16	2,0	Rh: 10,1	180
	0,45/2,15	1,745/6,45		6,45	120					
12	$RhCl_3$	A2	1:2	$LiBEt_3H$	THF	60	16	1,60	Rh:13,1	170
	0,45/2,15	1,164/4,3		6,45	120					
13	$RhCl_3$	A2	1:3	$LiBEt_3H$	THF	60	16	2,0	Rh:10,1	140
	0,45/2,15	1,745/6,45		6,45	120					
14	$RhCl_3$	A3	1:2	$LiBEt_3H$	THF	60	16	1,30	Rh: 16,2	110
	0,45/2,15	0,855/4,3		6,45	120					
15	$PdCl_2$	A2	1:2	$LiBEt_3H$	THF	25	16	2,64	Pd: 14,8	160
	0,71/4	2,17/8		5,6	300					
16	$PdCl_2$	A1	1:2	$LiBEt_3H$	THF	25	16	3,13	Pd: 13,35	280
	1,37/7,75	5,2/15,5		10,8	500					

Table 2: continuation 2

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
7	$PdCl_2$	A1	1:2	$LiBEt_3H$	THF	25	24	2,99	Pd: 13,7	260
	0,71/4	2,68/8		5,6	300					
8	$IrCl_3$	A1	1:3	$LiBEt_3H$	THF	60	16	2.10	Ir: 8,99	370
	0,51/1,71	1,72/5,13		5,16	100					
9	$PtCl_2$	A1	1:2	$LiBEt_3H$	THF	20	24	1,96	Pt: 58,93	420
	2,74/10,3	6,94/20,68		20,69	1100					
20	$PtCl_2$	A1	1:1	$LiBEt_3H$	THF	20	27	1,6	Pt: 32,64	350
	1,03/3,87	1,31/3,9		7,74	240					
21	$PtCl_2$	A1	1:0,5	$LiBEt_3H$	THF	20	27	1,46	Pt: 51,50	320
	1,03/3,87	0,655/1,95		7,74	240					
22	$PtCl_2$	A2	1:2	$LiBEt_3H$	THF	25	16	16,24	Pt: 22,09	160
	5,5/20,67	11,3/41,7		41,7	1200					
23	$PtCl_2$	A2	1:1	$LiBEt_3H$	THF	20	16	0,43	Pt: 22,6	170
	0,133/0,5	0,138/0,5		1,0	80					
24	$PtCl_2$	A2	1:0,5	$LiBEt_3H$	THF	20	16	0,35	Pt: 27,7	180
	0,133/0,5	0,068/0,25		1,0	80					

Table 2: continuation 3

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
25	$PtCl_2$	A3	1:2	$LiBEt_3H$	THF	20	108	2,0	Pt: 19,60	110
	0,857/3,23	2,35/6,45		6,45	200					
26	AgBr	A1	1:2	$LiBEt_3H$	THF	20	24	2,82	Ag:11,52	130
	1,36/5,1	3,5/10,2		10,2	550					

Table 3: Tenside-stabilized colloids of bimetals of the groups VIII-Ib of the periodic system by reduction with alkali BEt_3H in THF

No	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
1	$RuCl_3 \cdot FeCl_3$	A1	1:3	$LiBEt_3H$	THF	60	4	2,60	Ru: 8,84	210
	0,5/2,41 · 0,039/0,24	2,67/7,95		7,95	200				Fe: 0,38	
2	$RuCl_3 \cdot FeCl_3$	A1	1:3	$LiBEt_3H$	THF	60	4	2,45	Ru: 8,52	170
	0,5/2,41 · 0,078/0,48	2,91/8,67		8,67	200				Fe: 0,71	
3	$PtCl_2 \cdot CoCl_2$	A1	1:2	$LiBEt_3H$	THF	20	20	2,84	Pt: 17,6	280
	0,78/2,93 · 0,13/0,98	2,62/7,8		7,74	220				Co: 1,5	
4	$PtCl_2 \cdot CoBr_2$	A2	1:2	$LiBEt_3H$	THF	20	20	4,18	Pt: 12,4	200
	0,86/3,23 · 0,7/3,2	3,5/12,9		12,9	300				Co: 3,75	
5	$PtCl_2 \cdot CoBr_2$	A2	1:2	$LiBEt_3H$	THF	20	20	3,1	Pt: 20,1	210
	0,86/3,23 · 0,08/0,36	1,95/7,18		7,2	300				Co: 0,68	
6	$CODPtCl_2 \cdot CoBr_2$	A2	1:2	$LiBEt_3H$	THF	20	20	1,92	Pt: 14,5	190
	0,6/1,6 · 0,35/1,61	1,75/6,45		6,45	300				Co: 4,4	
7	$PtCl_2 \cdot NiBr_2$	A2	1:2	$LiBEt_3H$	THF	20	20	3,0	Pt: 20,9	185
	0,68/3,23 · 0,08/0,36	1,97/7,18		7,2	300				Ni: 0,7	
8	$PtCl_2 \cdot RhCl_3$	A1	1:2,25	$LiBEt_3H$	THF	40	24	2,66	Pt: 43,6	405
	2,31/8,72 · 0,61/2,91	8,78/26,17		26,16	1200				Rh: 7,55	

Table 3: continuation

No	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal/ l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
9	$PtCl_2 \cdot RhCl_3$	A1	1:2,55	$LiBEt_3H$	THF	50	28	3,60	Pt: 25,0	380
	1,80/6,79 - 1,41/6,74	11,56/34,45		34,0	1100				Rh:11,1	
10	$PtCl_2 \cdot RhCl_3$	A1	1:2,8	$LiBEt_3H$	THF	60	24	4,4	Pt: 13,89	370
	0,88/3,32 - 2,76/13,18	15,5/46,19		46,17	1200				Rh:16,3	
11	$PtCl_2 \cdot PdCl_2$	A1	1:2	$LiBEt_3H$	THF	20	24	5,13	Pt: 8,42	350
	1,03/3,88 - 0,68/3,88	5,2/15,5		15,5	550				Pd: 4,45	
12	$PtCl_2 \cdot IrCl_3$	A1	1:2.1	$LiBEt_3H$	THF	60	16	16,03	Pt: 17,3	430
	3,99/15,0 - 0,49/1,67	11,74/35,0		35,0	1200				Ir: 1,87	
13	$PtCl_2 \cdot IrCl_3$	A1	1:2,5	$LiBEt_3H$	THF	60	16	14,4	Pt: 8,8	410
	1,86/7,0 - 2,09/7,0	11,74/35,0		35,0	1200				Ir: 8,6	
14	$PtCl_2 \cdot IrCl_3$	A1	1:2,9	$LiBEt_3H$	THF	60	64	18,22	Pt: 1,4	400
	0,37/1,4 - 3,76/12,6	13,62/40,6		66,4	1200				Ir: 13,0	
15	$PtCl_2 \cdot IrCl_3$	A2	1:2,1	$LiBEt_3H$	THF	60	16	10,65	Pt: 15,3	190
	3,99/15,0 - 0,49/1,67	9,48/35,0		39,5	660				Ir: 1,6	

Table 4: Tenside-stabilized colloids of metals of the groups VIII-Ib of the periodic system by reduction with alkali metal boron hydrides in H_2O and alcohols, respectively

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	g	%	
	$RuCl_3x3H_2O$	A1 - NH_4Cl	1:3	$NaBH_4$	H_2O	40	2	1,24	Ru: 7,65	430
	0,36/1,74	1,75/5,21 - 0,28/5,21		0,2/5,21	150					
2	$RuCl_3x3H_2O$	A1 - NH_4Cl	1:3	$LiBH_4$	H_2O	40	2	0,42	Ru: 9,87	425
	0,31/1,17	1,18/3,51 - 0,19/3,51		0,08/3,51	160					
3	$RhCl_3x\ 3H_2O$	A1 - NH_4Cl	1:3	$NaBH_4$	H_2O	20	2	1,14	Rh: 8,25	450
	0,30/1,43	1,44/4,3 - 0,23/4,3		0,17/4,3	100					
4	$RhCl_3x\ 3H_2O$	A1	1:4	$LiBH_4$	Ethanol	0	24	7,3	Rh: 5,5	110
	1,4/5,3	7,2/21,2		0,34/15,9	150					
5	$PtCl_2$	A1	1:4	$NaBH_4$	H_2O	20	24	0,92	Pt: 9,8	355
	0,126/0,48	0,669/1,99		0,037/1,0	80					
6	$PtCl_2$	A1 - NH_4Cl	1:2	$NaBH_4$	H_2O	20	3	4,8	Pt.: 10,2	360
	1,4/5,3	3,6/10,6 - 0,4/7,9		0,4/10,6	100					
7	H_2PtCl_6 x 6 H_2O	A1	1:2	$NaBH_4$	H_2O	20	2	6,39	Pt: 12,1	320
	2,7/5,3	3,6/10,6		1,2/31,8	150					
8	H_2PtCl_6 x 6 H_2O	A1	1:4	$LiBH_4$	Ethanol	0	24	8,1	Pt: 9,5	120
	2,7/5,3	7,2/21,2		1,2/31,8	150					

Table 5: Tenside-stabilized colloids of bimetals of the groups VIII-Ib of the periodic system by reduction with alkali metal boron hydrides in H_2O and alcohols, respectively

No.	Metal salt g/mmole	Tenside g/mmole	Metal salt/-tenside molar ratio	Reduction agent mmole	Solvent ml	Reaction conditions T, °C	 t, h	isolated amount of product g	Metal content %	Water solubility in mg atom metal /l water
1	$H_2PtCl_6 \cdot CuCl_2 \times H_2O$	A1	1:3,84	$LIBH_4$	H_2O	20	2	7,05	Pt: 7,02	390
	1,35/2,65 - 0,11/0,66	4,3/12,7		0,38/17,0	150				Cu: 0,52	
2	$H_2PtCl_6 \cdot CuCl_2 \times H_2O$	A2	1:8	$LIBH_4$	H_2O	20	2	8,5	Pt: 6,0	170
	1,35/2,65 - 0,05/0,295	6,4/23,6		0,38/17	150				Cu: 0,2	
3	$RhCl_3 \times H_2O \cdot IrCl_3 \times H_2O$	A1	1:4	$LIBH_4$	H_2O	20	2	7,06	Rh: 2,7	340
	0,7/2,65 - 0,8/2,65	7,2/21,2		0,3/13,25	200				Ir: 5,0	
4	$RhCl_3 \times H_2O \cdot RuCl_3 \times H_2O$	A1	1:4	$LIBH_4$	H_2O	20	2	10,52	Rh: 2,3	410
	0,7/2,65 - 0,7/2,65	7,2/21,2		0,35/15,9	200				Ru: 2,3	
5	$RuCl_3 \times H_2O \cdot IrCl_3 \times H_2O$	A1	1:4	$LIBH_4$	H_2O	20	2	8,7	Ru: 2,6	450
	0,7/2,65 - 0,8/2,65	7,2/21,2		0,35/15,9	200				Ir: 4,9	
6	$H_2PtCl_6 \cdot RuCl_3 \times H_2O$	A1	1:4	$LIBH_4$	H_2O	20	2	10,36	Pt: 4,5	380
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,53/23,85	200				Ru: 2,2	
7	$H_2PtCl_6 \cdot RuCl_3 \times H_2O$	A1	1:4	$LIBH_4$	Ethanol	0	24	8,02	Pt: 4,7	120
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,53/23,85	200				Ru: 2,3	
8	$H_2PtCl_6 \cdot RhCl_3 \times H_2O$	A1	1:4	$NaBH_4$	H_2O	20	2	12,1	Pt: 4,3	360
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,9/23,85	200				Rh: 2,0	

Table 5: continuation

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions		isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	g/mmole	ml	T, °C	t, h	g	%	
8	$H_2PtCl_6 \cdot RhCl_3 \times H_2O$	A1	1:4	$LiBH_4$	H_2O	20	2	10,58	Pt: 4,5	355
	1,35/2,65 · 0,7/2,65	7,2/21,2		0,53/23,85	200				Rh: 2,2	
10	$H_2PtCl_6 \cdot PdCl_2 \times 2\ H_2O$	A1	1:4	$LiBH_4$	H_2O	20	2	11,1	Pt:4,5	310
	1,35/2,65 · 1,0/2,65	7,2/21,2		0,47/21,2	150				Pd: 2,5	
11	$H_2PtCl_6 \cdot Pd(NO_3)_2 \times H_2O$	C1		$LiBH_4$	H_2O	20	2	10,2	Pt: 2,0	140
	0,55/1,06 · 1,1/4,24	7,0/-		0,33/14,8	150				Pd: 4,3	
12	$H_2PtCl_6 \cdot IrCl_3 \times H_2O$	A1	1:4	$LiBH_4$	H_2O	20	2	10,34	Pt: 4,3	400
	1,35/2,65 · 0,8/2,65	7,2/21,2		0,47/21,2	200				Ir: 4,4	
13	$H_2PtCl_6 \cdot IrCl_3 \times H_2O$	A1	1:4	$LiBH_4$	H_2O	20	2	10,2	Pt: 4,4	420
	1,35/2,65 · 0,8/2,65	7,2/21,2		0,53/23,85	200				Ir: 4,5	

Table 6: Tenside-stabilized colloid of metals of the groups VIII-Ib of the periodic system by reduction with hydrogen in H_2O

No	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions			isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio		ml	T, °C	t, h	P, bar	g	%	
1	$RuCl_3 x 3H_2O$	A1	1:3	H_2	H_2O	60	10	1	0,43	10,98	370
	0,25/0,95	0,96/2,89			100						
2	$RuCl_3$	A1	1:3	H_2	H_2O	60	16	50	0,22	9,41	375
	0,16/0,78	0,79/2,34			100						
3	$RuCl_3 x 3H_2O$	A2 - K_2CO_3	1:3	H_2	H_2O	60	3	1	0,38	7,1	160
	0,22/0,84	0,68/2,53 - 0,23/1,67			80						
4	$Ru_2(OAc)_4$	A1	1:6	H_2	H_2O	60	16	50	0,41	8,78	210
	0,27/0,62	1,25/3,7			100						
5	$Ru(Acac)_3$	A1	1:3	H_2	H_2O	60	16	50	0,35	9,37	340
	0,39/0,97	0,98/2,91			100						
6	$RhCl_3 x 3H_2O$	A1	1:3	H_2	H_2O	20	2	1	1,02	11,40	330
	0,42/1,6	1,62/4,81			60						
7	$RhCl_3 x 3H_2O$	A2	1:3	H_2	H_2O	20	2	1	0,85	10,73	150
	0,40/1,52	1,24/4,57			100						
8	$PdBr_2$	A1 - Li_2CO_3	1:4	H_2	H_2O	20	3	1	9,6	5,3	290
	1,4/5,3	7,2/21,2 - 0,4/5,3			100						

Table 6: continuation 1

No	Metal salt g/mmole	Tenside g/mmole	Metal salt/-tenside molar ratio	Reduction agent	Solvent ml	Reaction conditions T, °C	t, h	P, bar	isolated amount of product g	Metal content %	Water solubility in mg atom metal / l water
9	H_2PtCl_6 x 6 H_2O	A1 - Na_2CO_3	1:4	H_2	H_2O	20	4	1	12,6	7,1	360
	2,7/5,3	7,2/21,2 - 3,4/31,8			100						
10	$PtCl_2$	A1 - K_2CO_3	1:4	H_2	H_2O	20	1,5	1	8,79	9,7	330
	1,4/5,3	7,2/21,2 - 0,73/5,3			100						
11	$PtCl_2$	A1 - K_2CO_3	1:4	H_2	H_2O	20	3	1	8,5	10,1	310
	1,4/5,3	7,2/21,2 - 0,73/5,3			100						
12	$PtCl_2$	A1 - Na_2CO_3	1:4	H_2	H_2O	20	1,5	1	9,0	10,8	350
	1,4/5,3	7,2/21,2 - 0,56/5,3			100						
13	$PtCl_2$	A1 - Li_2CO_3	1:4	H_2	H_2O	20	2	1	140	10,3	370
	21/79,6	108/318 - 6/79,5			1500						
14	$PtCl_2$	A1 - Li_2CO_3	1:2	H_2	H_2O	20	2	1	73,7	17,9	450
	21/79,5	54/159 - 3/39,75			1500						
15	$PtCl_2$	A1 - Li_2CO_3	1:4	H_2	H_2O	20	3	1	8,4	10,7	380
	1,4/5,3	7,2/21,2 - 0,4/5,3			100						
16	$PtCl_2$	A1 - Li_2CO_3	1:2	H_2	H_2O	20	2	1	6,1	16,4	440
	1,4/5,3	3,6/10,6 - 0,2/2,65			100						

Table 6: continuation 2

No	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions			isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio		ml	T, °C	t, h	P, bar	g	%	
17	$PtCl_2$	A1 - Li_2CO_3	1:4	H_2	H_2O	20	1,5	1	9,5	10,4	380
	1,4/5,3	7,2/21,2 - 0,4/5,3			100						
18	$PtCl_2$	A1 - LiBr	1:4	H_2	H_2O	20	3	1	9,7	9,8	360
	1,4/5,3	7,2/21,2 - 0,5/5,3			100						
19	$PtCl_2$	A1 - LiBr	1:2	H_2	H_2O	20	3	1	6,1	16,9	370
	1,4/5,3	3,6/10,6 - 0,25/2,65			100						
20	$PtCl_2$	A2 - Li_2CO_3	1:8	H_2	H_2O	20	3	1	14,1	7,1	160
	1,4/5,3	11,5/42,4 - 0,8/10,6			100						
21	$PtCl_2$	A4 - Li_2CO_3	1:8	H_2	H_2O	20	3	1	17,3	5,7	110
	1,4/5,3	14,6/42,4 - 0,8/10,6			100						
22	$PtCl_2$	B1 - Li_2CO_3	1:4	H_2	H_2O	20	3	1	25,1	4,1	105
	1,4/5,3	21,7/21,2 - 0,4/5,3			100						
23	$PtCl_2$	D1 - Li_2CO_3		H_2	H_2O	20	4	1	9,5	10,6	130
	1,4/5,3	7/- - 0,4/5,3			100						
24	$PtCl_2$	C1 - Li_2CO_3		H_2	H_2O	20	2	1	9,7	10,6	145
	1,4/5,3	7/- - 0,4/5,3			100						

Table 6: continuation 3

No.	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions			isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio		ml	T, °C	t, h	P, bar	g	%	
25	$PtCl_2$	E1 - Li_2CO_3	1:4	H_2	H_2O	20	4	1	11,5	8,9	110
	1,4/5,3	8,3/21,2 - 0,4/5,3			100						
26	$PtCl_2$	F1 - Li_2CO_3		H_2	H_2O	20	3	1	13,7	6,8	110
	1,4/5,3	7,2/- - 0,4/5,3			200						
27	$PtCl_2$	B2 - Li_2CO_3	1:4	H_2	H_2O	20	3	1	10,8	9,1	105
	1,4/5,3	7,2/21,2 - 0,4/5,3			100						

Claims

1. Process for producing tenside-stabilized colloids of mono- and bimetals of the groups VIII and Ib of the periodic system having particles sizes of 1-10 nm, characterized in that metal salts are reacted in the presence of strongly hydrophilic tensides selected from the group consisting of amphiphilic betaines, cationic tensides, fatty alcohol polyglycol ether, polyoxyethylene-carbohydrate-fatty alkylester and/or anionic tensides and/or amphiphilic sugar tensides, in THF, alcohols, or directly in water, with chemical reduction agents such as hydrides, hydrogen or alkali formate, between 0°C and 100°C at normal pressure, optionally by adding alkali carbonates and/or ammonium chloride, and that the precursors are isolated from the thus prepared solutions of >100 mg atom metal/l.

2. Process for producing carrier supported metal colloid catalysts by using preformed, tenside-stabilized mono- and bimetalic colloids of metals of the groups VIII and Ib of the periodic system according to claim 1, characterized in that the colloids stabilized by tensides are used in the form of solutions for adsorptive coverage of carriers.

3. Tenside-stabilized colloids of mono- and bimetals of the groups VIII and Ib of the periodic system having particles sizes of 1-10 nm, characterized by a surface area coverage with strongly hydrophilic tensides, selected from the group consisting of amphiphilic betaines, cationic tensides, fatty alcohol polyglycol ether, polyoxyethylene-carbohydrate-fatty alkylesters and/or anionic tensides and/or amphiphilic sugar

tensides, which are obtainable by chemical reduction with reduction agents such as hydrides, hydrogen or alkali formate, of metal salts in the presence of tensides between 0°C and 100°C at normal pressure, optionally by adding alkali carbonates and/or ammonium chloride, and isolation of the precursor from the thus prepared solutions of >100 mg atom metal/l.

4. Colloids according to claim 3, characterized in that the strongly hydrophilic tensides are selected from particularly nonionic tensides having HLB-values of > 8.

5. Use of the tenside-stabilized colloids of mono- and bimetals, obtainable according to claims 1 and 2, as precursors for producing metal colloid-heterogeneous catalysts by adsorption from aqueous solution onto inorganic or organic carrier materials..

6. Use according to claims 1 to 5, characterized in that the metal colloids are used in concentrations of up to 25 percent per weight of metal content in relation to the total weight of the solution.

7. Use of the metal colloid-heterogeneous catalysts Pt-A-activated carbon, Pd-A-carbon, Pd/Pt-A-carbon, obtainable according to claim 5, for the partial oxidation of primary alcohol functionalities in carbohydrates.

8. Use according to claims 1 to 5, characterized in that carbon carriers, ceramic oxides, carbonates, sulfates or zeolites in the form of powders or formed bodies are used as carriers.

9. Use of the palladium colloid-A-carbon-catalysts, respectively, Pd-colloid-$CaCO_3$-catalysts, obtainable

according to claim 5, for the selective cis-hydrogenation of C-C- triple bonds.

10. Use of the heterogeneous catalysts on oxides of the metal oxides of the lanthanoids, prepared according to claim 5, as carrier for the selective hydrogenation of benzene to cyclohexene.

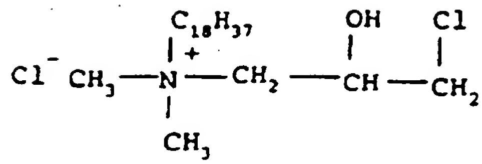
11. Use of the rhutenium-lanthanoidoxide-heterogeneous catalysts, obtainable according to claim 10, for the selective hydrogenation of benzene to cyclohexene.

12. Mono- and bimetalic colloids (particle size 1-10 nm) from Cu, Ru, Rh, Pd, Ir, Pt, Ag, Ru/Fe, Pt/Co, Pt/Rh, Pt/Pd, Pt/Ir, Pt/Cu, Pt/Ru, Rh/Ir, Rh/Ru, Ru/Ir which are alkali-free stabilized hydrophilically with 3-(N,N-dimethyldodecyl amommonium)propane sulfonate, and being soluble in water at a concentration of > 100 mg atom metal/l.

13. Mono- and bimetalic colloids (particle size 1-10 nm) from Ru, Rh, Pd, Pt, Pt/Co, Pt/Ni, Pt/Ir, Pt/Cu, which are hydrophilically stabilized with lauryldimethyl carboxymethyl ammonium betaine, and being soluble in water at a concentration of > 100 mg atom metal/l.

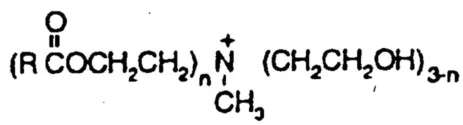
14. Ru- and Pt-colloids (particle size 1-10 nm) which are hydrophilically stabilized with cocoamidopropyl betaines, and being soluble in water at a concentration of > 100 mg atom metal/l.

15. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with



and being soluble in water at a concentration of > 100 mg atom metal/l.

16. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with



R = alkyl radical of partially hydrogenated palm grease, and being soluble in water at a concentration of > 100 mg atom metal/l.

17. Mono- and bimetalic colloids (particle size 1-10 nm) from Ni, Co, Pt, Pt/Pd which are hydrophilically stabilized with polyoxyethylene laurylether, and being soluble in water at a concentration of > 100 mg atom metal/l.

18. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with polyoxyethylene sorbitan monolaurat, and being soluble in water at a concentration of > 100 mg atom metal/l.

19. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with Na-cocoamidoethyl-N-hydroxyethyl-glycinate, and being soluble in water at a concentration of > 100 mg atom metal/l.

20. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with alkylpolyglycoside, and

being soluble in water at a concentration of > 100 mg atom metal/l.

21. Carrier fixed heterogeneous metal colloid catalysts comprising mono- and bimetals of the groups VIII and Ib of the periodic system, obtainable by the use of solutions of preformed tenside-stabilized mono- or bimetal colloids of said metals by adsorptive coverage of said carriers.

22. Catalysts according to claim 21 comprising inorganic or organic carrier materials.

23. Catalysts according to claim 21, characterized in that the carrier materials comprise carbon carriers, ceramic oxides, carbonates, sulfates or zeolites in the form of powders or formed bodies.

24. Catalysts according to one or more of the claims 21 to 23 characterized by a coverage comprising oxides of lanthanoide elements, in particular lanthanum oxide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/04803

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J37/03 B01J37/02 B01J13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 147 841 (WILCOXON JESS P) 15 September 1992 see claim 1 ---	1
X	DE,A,44 10 353 (YUKONG LTD) 29 September 1994 see page 3, line 65 - page 4, line 40 ---	1-3,5,8, 21-23
X	EP,A,0 580 559 (TANAKA PRECIOUS METAL IND ;STONEHART ASS INC (US)) 26 January 1994 see claim 1	1,2
Y		7

Y	US,A,4 136 059 (JALAN VINOD M ET AL) 23 January 1979 see claim 1; example 1 ---	7
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
7 May 1996	13.05.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Thion, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,212 035 (WALTER ALBERT PATRICK) 6 March 1924	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 95/04803

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		DE-C- 434211	
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